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TECHNOLOGY STUDY ON PIEZOELECTRIC MATERIALS

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W.B. Harrison
A.G. Thalheimer
Honeywell, Inc.
Avionics Division
P.O. Box 11563
St. Petersburg, Florida 33733

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The use of Honeywell's ring laser gyros technology is being considered for maneuvering reentry vehicle guidance where hostile nuclear radiation environments may be encountered by the ring laser gyro and its path length control (PLC) transducer. In an effort jointly sponsored by SAMSO and DNA, Honeywell and IRT[1] performed tests and analytical analysis on an operating laser gyro. It was shown that some "mode hopping" transient motions were produced by the PLC transducer when subject to x-ray exposure. The materials

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20. ABSTRACT (Continued)

used in the PLC transducer were analyzed and the high Z lead zirconate-lead titanate (PZ-PT) materials used in the transducer were considered as a partial cause of this phenomena. This program was therefore initiated to determine if lower Z materials, free of lead, were suitable replacements for the PZ-PT used in the PLC driver section of the transducer.

PREFACE

This contract funded by the Defense Nuclear Agency covers the technical effort performed before 26 June 1978 through 31 December 1978 to investigate techniques to improve the radiation resistance and stability of the piezoelectric actuators used for mirrors in laser gyros and similar devices. This effort primarily considers nonlead piezoelectric on electrostrictive materials which could replace the currently used lead zirconate-lead titanate ceramic.

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INTRODUCTION

BACKGROUND

The typical Honeywell ring laser gyro is built, as shown in Figure 1, from a very low thermal expansion, fused silica type material CERVIT which is used for the primary block. The primary function of the block is to provide a high quality gas container and an ultrastable aperture and mounting surfaces for the various mirrors, anodes and cathodes attached to the block. The anodes and cathodes of course initiate and maintain the two helium-neon laser beams traveling in opposite directions. Two stationary and one movable mirror are used to provide an active closed-loop path length control system to maintain a constant operating point for the gyro. The control loop functions so that the gyro output power, monitored by one of the photoconductive detectors, is continuously maximized. Changes in the gyro path length result in variations in gyro power output and scale factor. The relationship between gyro scale factor, power output and path length are shown in Figures 2 and 3. The variations in scale factor are repetitive from mode to mode; however, there is an absolute shift in scale factor of approximately three parts per million per mode.

The moveable mirror or path length control (PLC) transducer is typically designed as shown in Figure 4. The three main components of the PLC transducer are: the fused silica (CERVIT) transducer with its movable mirror surface held in place by the thick CERVIT diaphram; the driver section which is composed of two discs of PZ-PT mounted on a CERVIT plate; and an Invar mounting nut and bolt to hold the driver to the mirror section. As the voltage applied to the driver is increased or decreased the driver deflects and forces the mirror forward or backward respectively.

PLC TRANSDUCER STABILITY TO X-RAYS

Three primary areas of concern, identified in an earlier investigation[1], relate to the PLC transducer. These are 1) the path length changes caused by x-ray

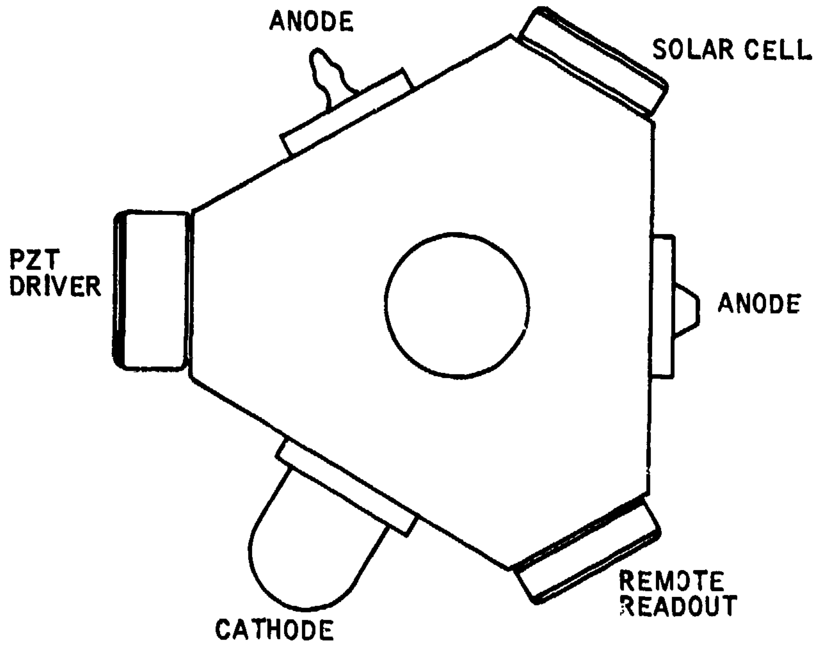


Figure 1. Laser gyro block assembly.

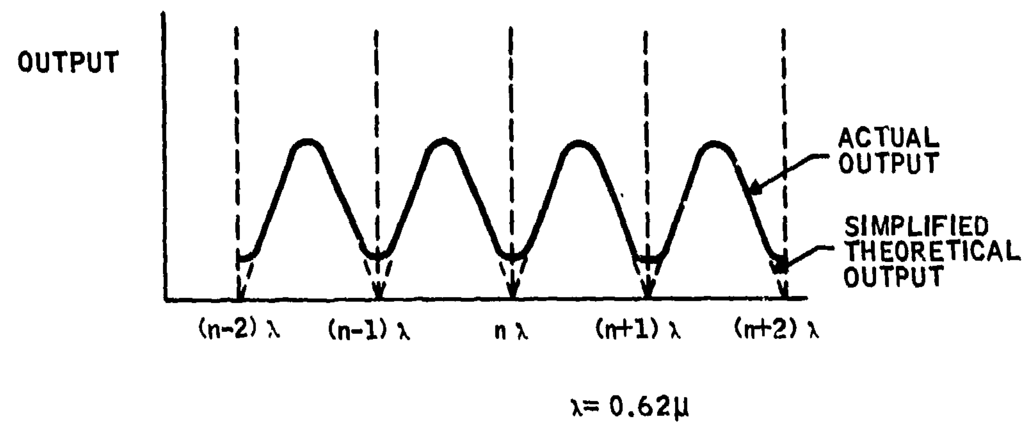


Figure 2. Laser gyro output versus path length.

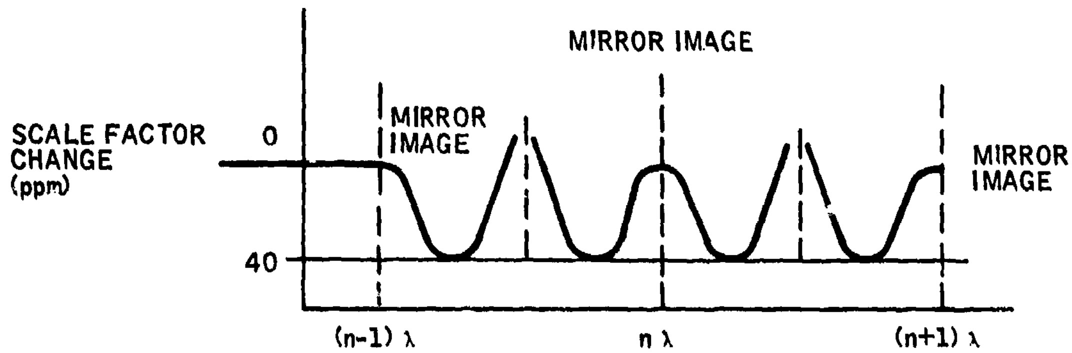


Figure 3. Laser gyro scale factor versus path length.

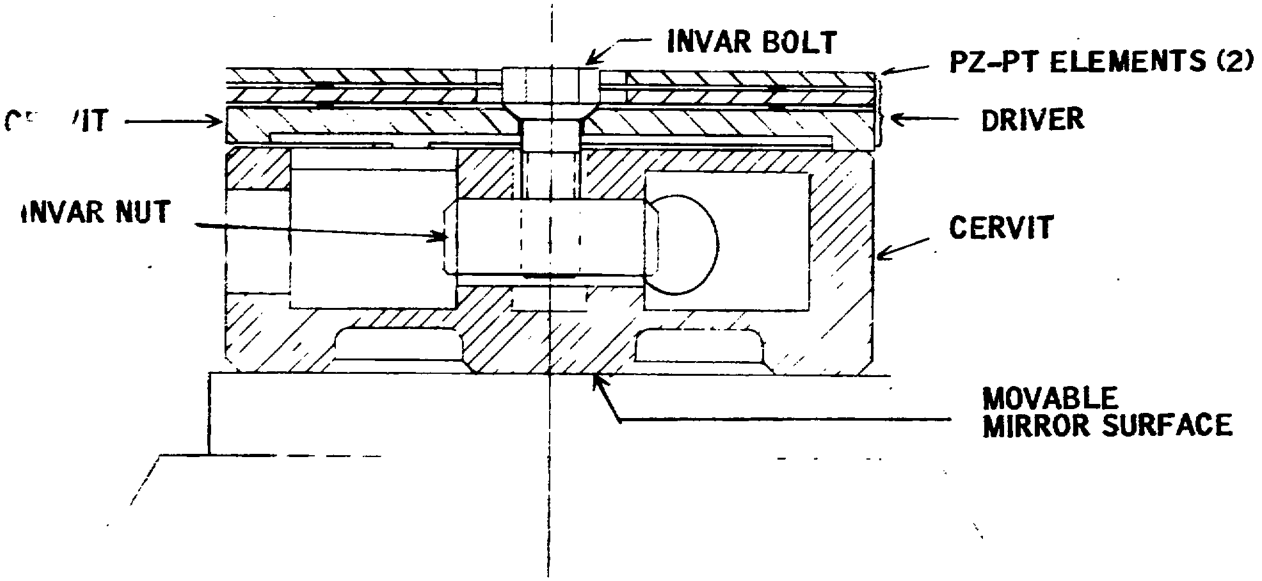


Figure 4. PLC transducer - present configuration.

heating of the PLC transducer assembly, 2) the recovery time of the PLC subsystem from high intensity x-radiation and 3) the potential for unidentifiable mode changes caused by x-ray heating.

The first response of the PLC transducer assembly to the nearly instantaneous temperature rise produced by x-ray exposure is a discrete spectrum of millisecond type mechanical oscillations as illustrated in Figure 5. The primary source of these oscillations is the PZ-PT driver element excited by energy disposition from x-rays. The PLC transducer assembly also produces a long term transient path length change lasting for many seconds as in Figure 5. The initial magnitude of the transient may exceed one wavelength (λ). The time duration of this transient is determined by the equilibration characteristics of the transducer and cooling provided.

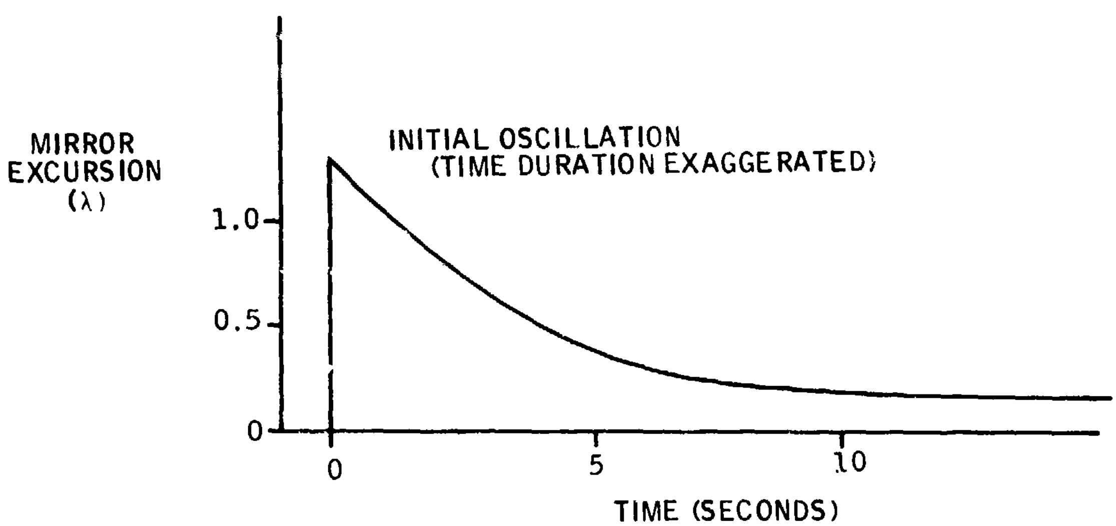


Figure 5. Path length transducer x-ray response.

When the PLC transducer senses short term radiation induced transients, which are greater than a half wavelength, the subsystem may lock the gyro into an undefined operating mode and errors in scale factor may exceed six parts per million. Long term transient charges of 30 seconds were shown to produce small angular (0.1°) roll errors; however, these are well within the error budget and the recovery time of the PLC subsystem was found to sufficiently quick to maintain angular error buildup within bounds. It was therefore concluded that the errors in scale factor should be brought under control.

The most effective means of correcting this problem would be to redesign the PLC transducer to reduced the average atomic mass (Z) of the materials used in the construction of the driver.

SECTION 2
EXPERIMENTAL EFFORT

This section presents the experimental approach, discussion and results of the experimental effort on this program to define lower molecular weight materials for the PLC driver and to arrive at a more stable transducer design for using these materials.

APPROACH

The objective of this study on "Non-Leaded Piezoelectric Materials" is to improve the radiation resistance stability of the piezoelectric drivers used on the path length control PLC transducer for laser gyros. The initial task was a literature search and material selection to identify low atomic number (Z) non-lead containing piezoelectric or electrostrictive materials for further study. The materials identified were then evaluated at high voltages to determine their electric field versus displacement characteristics. Based on the activity obtained, several materials and conceptual designs for PLC drivers and transducers were examined for a follow-on study program.

LITERATURE SEARCH

Five primary sources of literature were reviewed for articles on ferroelectric and dielectric materials with high electromechanical displacements. These included 1) International Aerospace Abstracts, 2) U.S. Government Research and Development Reports, 3) Ceramic Abstracts, 4) Ferroelectrics and 5) books devoted to ferroelectric materials.

Ferroelectrics, an international journal, contains two continuously updated bibliographies, one by Lang, "Literature Guide to Pyroelectricity" and the other by Toyoda, "Bibliography of Ferroelectrics." Toyoda gives a listing of articles, books and conference proceedings dealing with ferroelectrics and related materials published throughout the world. About 9000 listings for the last six years were

reviewed for new materials which did not contain lead or other elements with an atomic number greater than 56 (Barium) as a primary constituent.

The materials found, which had sufficient data reported to determine their electromechanical behavior, are given in Table 1 according to their average atomic mass and compared to the $PbZrO_3$ - $PbTiO_3$ presently used in the PLC transducer. These 35 materials can be broken down into five classes: 1) perovskite-type oxides, 2) aqueous solution grown crystals, 3) semiconductive compounds, 4) other oxides and 5) organic polymeric compounds.

In order to avoid confusing molecular mass with atomic mass, consider TGS. The molecular mass of this chemical compound is large, even though it is composed of a large number of light elements. Triglycine Sulfate (TGS) $(NH_3\ CH\ OOH)_3\ SO_4$, which has a 32 atom molecule for a molecular mass of 321, has an average atomic mass (per atom) of only 10. In x-ray vulnerability considerations, it is desirable to reduce the temperature rise with its commensurate thermal distortion. There are two ways to do this: 1) select a low atomic number (Z) material, because for a given x-ray dosage different atoms extract energy about as Z^4; or 2) select a material with a high heat capacity to minimize the temperature rise associated with the deposition of x-ray energy. In essence, the room temperature heat capacity of most materials is described by the equipartition theorem, also called the law of Dulong and Petit. This rule says that the internal energy of any atom in a solid is proportional to is 3 kT, where k is the Boltzmann's constant, so the heat capacity of a mole of atoms is 3 rN kT which is also 3 rR (per mole) where r is the number of atoms per molecule, and R is the universal gas constant (1.98 cal/mole°). This means for example, that although water (H_2O) and Sodium (Na) have very similar molecular masses (18 vs. 19) and hence will extract nearly equal amounts of energy per molecule from a given x-ray, they will not heat equal amounts. Water, which has 3 atoms per molecule, will have a heat capacity of about 16 cal/mole °C = 1 cal/gm °C $\approx$ 0.3 cal/gm-°C. Since water's heat capacity is three times that of sodium, sodium would be heated three times as much as water by identical x-rays.[24]

Perovskite-Type Oxides

Sixteen of the materials in Table 1 have the general formula ABO_3 which normally have a distorted perovskite, simple cubic structure. The A-type cation at the

Table 1. Piezoelectric properties of materials. (sheet 1 of 2)

Form	Material	Mol. Weight	Average Atomic Mass	Curie Temp. (°C)	Density gm/cc	Dielectric Constant	Piezoelectric Coupling	Piezoelectric Strain Constant m/v (10^{-12})	Piezoelectric Voltage Constant V/M (10^{-3})	Piezoelectric Compliance $m^2/N(10^{-12})$	Reference
S.C.	$(NH_3)h_2PO_4$ (ADP) (0° Z-Cut)	99	9	125	1.80	32	0.32	48	354	53	2, 3
S.C.	$(NH_3CH\ OOH)_3SO_4$ TGS	321	10	46							4
S.C.	$NaKC_4H_4O_6 \cdot 4H_2O$ (45° X-Cut)	282	10	45	1.77	350	0.73	275	98	67	3
S.C.	(Rochelle Salt) (45° Y-Cut)	282	10	45	1.77	10	0.29	29	290	99	3
Organic	$(CH_2CH_2)_n$ Polyvinylidene	$(64)_n$	11	110	1.8	11	0.16	14	140		5, 6
S.C.	BeO	25	13		3.01	8	0.02	0.2		[illegible] 3	7
S.C.	$Li_2SO_4\ H_2O$(LH) (0° Y-Cut)	128	13	100	2.06	10	0.38	16	175	20	2, 8
S.C.	$K\ H_2\ PO_4$ (KDP) (0° Z-Cut)	136	17	150	2.34	21	0.12	21	102	49	2, 3
S.C.	$H_4NaMn_3Al_6B_3Si_6O_{31}$ (Tourmaline)	1050	19		3.10	1700	0.10	2			3, 9
S.C.	Quartz (SiO_8) (Y-Cut)	60	20	550	2.65	5	0.10	2	58	12	3
S.C.	AlN	41	21		3.26	9	0.20	6	61	2.8	8
S.C.	RbH_2PO_4 (RbDP)	183	23		2.8	248		3		23	10
S.C.	$LiGaO_2$	109	27		4.19	9	0.25	8	93		3
S.C.	$Li\ NbO_3$	148	30	1210	4.70	30	0.16	6	23	5.0	8
S.C.	$K_3Li_2Nb_5O_{15}$	836	33	420		120	0.64				11
Ceramic	$Na_{0.8}Cd_{0.1}NbO_3$	171	34	240		2000	0.42	200	11		1

Table 1. Piezoelectric properties of materials. (sheet 2 of 2)

Form	Material	Mol. Weight	Average Atomic Mass	Curie Temp. (°C)	Density gm/cc	Dielectric Constant	Coupling	Strain Constant m/v (10^{-12})	Voltage Constant V/M (10^{-3})	Compliance m^2/N (10^{-12})	Reference
Ceramic	$Na_{0.5}K_{0.5}NbO_3$	172	34	420	4.46	496	0.46	127	29	10	12, 13
S.C.	$LiIO_3$	192	36	256	4.47	6	0.51				14
S.C.	$Sr_4K\ LiNb_{10}O_{30}$	1806	39			870	0.48				15
S.C.	ZnO	81	41		5.68	11	0.41	11	109	6.9	8, 16
S.C.	$K_3Li_2(Ta_{0.46}Nb_{0.54})_5O_{15}$	1038	42	160		360	0.50				11
S.C.	$Ba_2NaNb_5O_{15}$	1002	44		5.3	51	0.57	37	82	8.3	17
S.C.	$(Sr_{0.5}Ba_{0.5})Nb_2O_6$	396	44	120		400	0.54	- 20			16, 18
Ceramic	$BaTiO_3/CaTiO_3$ [illegible]/5	228	46	120	5.50	1100	0.45	140	14	9.1	19
Ceramic	$BaTiO_3/CaTiO_3/PbTiO_3$ 85/7.5/7.5	231	46	145	5.25	600	0.30	100	19	9.4	19
Ceramic	$BaTiO_3/ZrO_3$ 98/2	231	46	103		1075		- 70	8		1
S.C.	$BaTiO_3$	233	46	120	5.7	1900	0.49	191	11		1, 12
S.C.	$LiTaO_3$	236	47	630	4.19	45	0.18	3	21	4.4	8, 20, 16
S.C.	ZnS	97	49		4.09	8	0.03	2			8
S.C.	$SrTeO_3$	263	53		4.32	97	0.34	42	282	23	21
S.C.	$KTaO_3$	265	53	-260							
Ceramic	$Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ (PZ-PT)	326	65	300	7.6	1250	0.65	230	25	15	19
S.C.	CdS	144	72		4.82	92	0.26	10	113	21	22
S.C.	$GaAs$	145	73		5.31	11	0.07	3		1.2	23
S.C.	$CdSe$	191	86		5.67	11	0.19	8	83	17	2, 16
S.C.	$ZnTe$	193	87		5.64	10	0.02	0.5			8
S.C.	$SbSI$	231	94	20		2200	0.87				8

corners of a cube is coordinated with twelve oxygen ions at the center of each face and the B-type cation at the body center is coordinated with six oxygen ions. These can also be subdivided into three groups according to the valence state of the A and B-site elements such as $A^{+1}B^{+5}O_3$, $A^{+2}B^{+4}O_3$ and complex mix valence state of these sites. The ferroelectric compounds formed normally have rhombohedral, tetragonal or orthorhombic symmetry. In the following discussion we will discuss the materials according to their valence state and not their crystallographic state. Indeed, some of the materials ($LiNbO_3$ and $LiTaO_3$) do not have the perovskite-type structure. The first group are seven $A^{+1}B^{+5}O_3$ materials which include $LiNbO_3$, $(Na_{0.5}K_{0.5})NbO_3$, $LiTaO_3$, $KTaO_3$, $K_3Li_2Nb_5O_{15}$, $LiIO_3$ and $K_3Li_2(Ta_{0.46}Nb_{0.54})_5O_{15}$. The ceramic form of sodium potassium niobate has good piezoelectric properties, a high Curie temperature and about half the average atomic mass as the presently used PZ-PT. Lithium niobate has been used extensively as a single crystal because of its very high Curie temperature (1210°C) and its acoustic surface wave properties. Large single crystals are readily available but have a fairly high price and poor piezoelectric properties. The other five materials either have poor piezoelectric properties or insufficient information was available at this time to judge the suitability of their properties for the PLC displacement transducer.

Six $A^{+2}B^{+4}O_3$ compounds were identified which included four types of $BaTiO_3$, $(Sr_{0.5}Ba_{0.5})Nb_2O_6$ and $SrTeO_3$ as well as the presently used PZ-PT. Two of the barium titanate ceramic materials have been used extensively as piezoelectric ceramics, predating PZ-PT by about ten years. Two of the $BaTiO_3$ modifications contain $CaTiO_3$ or $CaTiO_3$ and $PbTiO_3$ and are produced at Honeywell as Type 101 and 113 $BaTiO_3$, respectively. Both have good piezoelectric behavior and were used as displacement transducers prior to the discovery of the more active PZ-PT in other devices (not the laser gyro). Their average atomic mass is about 30 percent less than PZ-PT, but they have a low Curie temperature. Single crystal $BaTiO_3$ has better properties but is difficult and not practical to produce in large shapes. The other two materials offer no advantage in piezoelectric properties and have higher molecular weights.

Three complex ABO_3 materials, where compensating valencies are used to achieve either $A^{+1}B^{+5}O_3$ or $A^{+2}B^{+4}O_3$ compounds, were identified as $(Na_{0.8}Cd_{0.1})NbO_3$, $Ba_2Na\ Nb_5O_{15}$ and $Sr_4\ K\ Li\ Nb_{10}O_{30}$. While the last two of these contain lighter elements, their average atomic mass was sufficiently high to rule them out as candidate PLC materials. The $Na_{0.8}Cd_{0.1}NbO_3$ ceramic material is of interest

because it does have a high Curie temperature and good piezoelectric properties. In fact, its strain constant is second best to all of the materials considered as a substitute for the PZ-PT currently used. This material is not now currently commercially produced and a production process would have to be developed before this material could be applied to displacement transducers.

Aqueous Solution Growth Crystals

Six of the materials described in Table 1 were derived by the aqueous solution growth of single crystals. These were attractive because their average atomic mass was about 80 percent less than PZ-PT. They include ammonium dihydrogen phosphate (ADP), potassium dihydrogen phosphate (KDP), Rubidium dihydrogen phosphate (RDP), sodium potassium tartarate(Rochelle salt), triglycine sulfate (TGS), and lithium sulphate (LH). Rochelle salt had the highest piezoelectric constants and has been used extensively in various older transducer designs, however, it has two primary drawbacks. Its Curie temperature is only 45°C and its piezoelectric output is very water sensitive. The strain constant for those crystals, which are 45° x-cut, are found to be better than $(Na_{0.8}Cd_{0.1})\ NbO_3$ reported above and almost equal to PZ-PT. TGS and Rochelle salt have average atomic mass about one third that of sodium cadmium niobate reported above. The other materials, while much lower in molecular weight, have relatively poor piezoelectric strain constants. TGS also contained no elements with an atomic number greater than 16 (Sulfur).

Semiconducting Compounds

Eight semiconducting compounds are cited in Table 1, AlN, ZnO, ZnS, CdS, GaAs, CdSe, ZnTe and SbSI. All of these have a lower molecular weight than PZ-PT. For instance, the average atomic mass varied from 21 for AlN to 94 for SbSI as opposed to 65 for PZ-PT. The piezoelectric strain constants of these materials are less than 5 percent of that produced by PZ-PT even though SbSI had a high coupling coefficient of 0.67.

Other Oxides

Four other oxides, including quartz, probably the most widely used transducer material, were listed in Table 1. In addition to quartz, BeO, $LiGaO_2$ and Tourmaline, a complex silicate, were included. Tourmaline (like quartz) is a naturally occuring crystal which was one of the first piezoelectric materials identified. Again, while these contain low molecular weight elements, they have very weak piezoelectric strain constants.

Polymeric Compounds

Recently, (18, 19) the piezoelectric behavior of several polymeric materials have been studied and found to exhibit significant piezoelectric properties. One of the more promising materials identified is polyvinylidene fluoride (PVF_2) which is $(CH_2 + CF_2)n$. The properties of this material are also given in Table 1. Even though this material has been shown to be quite useful as a mechanical to electrical hydrophone type transducer material, it has very poor ability to convert electrical energy into mechanical motion as necessary for the PLC transducer.

PROCEDURES

Ten of the 35 materials discussed above were selected for further test, evaluated and then compared to the present PZ-PT used. Those selected, and their class, are included in Table 2. None of the polymeric and semiconducting type materials were selected for further study because of their low piezoelectric strain constants. The first three materials selected are ceramic type materials which are standard materials produced at Honeywell. The $(Sr_{0.5}Ba_{0.5})Nb_5O_{15}$ and K Ta O_3 single crystal materials were grown by Liu (9, 15) at our Corporate Materials Science Center. The TGS and $LiGaO_2$ were obtained from Phillips Research and the Rochelle salt and $LiNbO_3$ were produced by Clevite and Crystal Technology, respectively. The $(Na_{0.8}Cd_{0.1})$ NbO_3 and $(Na_{0.5}K_{0.5})$ NbO_3 are ceramic materials which require a detailed compositional development effort; therefore, samples of these were not available for further testing.

Table 2. Experimental Materials

Material	Average Atomic Mass	Source	Class and Form: Perovskite $A^{+1}B^{+5}O_3$	Class and Form: Perovskite $A^{+2}B^{+4}O_3$	Class and Form: Perovskite Complex	Class and Form: Aqueous Solution Grown	Class and Form: Other Oxide	Shape: "Z" Axis	Shape: "X" Axis	Shape: "Y" Axis
Hot Pressed K-13 PZ-PT	65	Honeywell		C				0.400	0.180	0.180
$BaTiO_3/CaTiO_3$ Type 101	46	Honeywell		C				0.400		
$BaTiO_3/CaTiO_3/PbTiO_3$ Type 113	46	Honeywell		C				0.400		
$(Sr_{0.5}Ba_{0.5})Nb_5O_{15}$	44	Honeywell		S.C.				0.400	0.165	0.127
$LiNbO_3$	30	Crystal Tech	S.C.					0.223	0.195	0.539
$(Na_{0.5}K_{0.5})NbO_3$	34	*	C						*	
$K Ta O_3$	53		S.C.					0.200	0.200	0.250
$(Na_{0.8}Cd_{0.1})NbO_3$	34	*			C				*	
Rochelle Salt	10	Clevite				S.C.		0.631	0.431	0.319
TGS	10	Phillips				S.C.		0.225	0.295	0.454
$LiGaO_2$	27	Phillips					S.C.	0.245	0.220	0.396

C - Ferroelectric Polycrystalline Ceramic

SC - Single Crystal

* - Not commercially available

One to eight samples of eight of the materials given above were prepared into field versus displacement test specimens. Each sample was shaped to the size indicated in Table 2 by diamond sawing and grinding. The long dimension (z-axis) of all samples was the growth or initial poling direction of all materials. Fired silver electrodes were applied to the PZ-PT and $BaTiO_3$ samples prior to poling each material at about 60 volts/mil at 145° and 140°C, respectively. Conductive epoxy-silver or aluminum foil electrodes were used on the other materials when the field was applied in the transverse, d_{15} direction. Side electrodes were applied and leads were attached after removing the top and bottom polarization electrodes.

The first application of d.c. voltage was applied in the same direction as the poling field while the displacement was measured as shown in Figure 6. A positive voltage of at least 37.5 volts/mil was applied, reversed to zero and then to a negative voltage to obtain the depoling switching voltage. Five positive voltage cycles were then applied from 0 to +37.5 volts/mil to stabilize the displacement. The percent extension was measured at 35 volts/mil, the "d" constant was calculated for this field and then reported in Table 3.

The high voltage power supply had an automatic triangle ramp where the full cycle with change of polarity takes one minute. An automatic half cycle with no change of polarity could also be run. The peak voltage could also be set prior to the automatic cycle. To calibrate the unit, a dial indicator, the transducer amplifier, and the x position of the recorder pen were zeroed. Voltage on the ceramic was raised manually to give a dial indicator deflection of 0.0005 inch . Sensitivity of transducer amplifier and x- calibration of recorder were adjusted to give a known travel to the recorder pen. Most studies were run with a sensitivity of 20 cm = 0.0005 inch.

Automatic cycles were normally run without the dial indicator because its pressure was found in some cases to influence the shape of the loop. The sample was then only under the dead weight of the plexiglas rod (about 90 gm) plus whatever pressure was exerted by the transducer probe.

Data obtained in this manner is similar to d_{33} where the extension is measured in the same direction as the voltage. A second set of data was then determined where the voltage was applied to the length of the sample and extension was measured perpendicular to the poling direction (d_{31}). The end electrodes were removed and air cured electrodes were applied on two sides perpendicular to the original poling

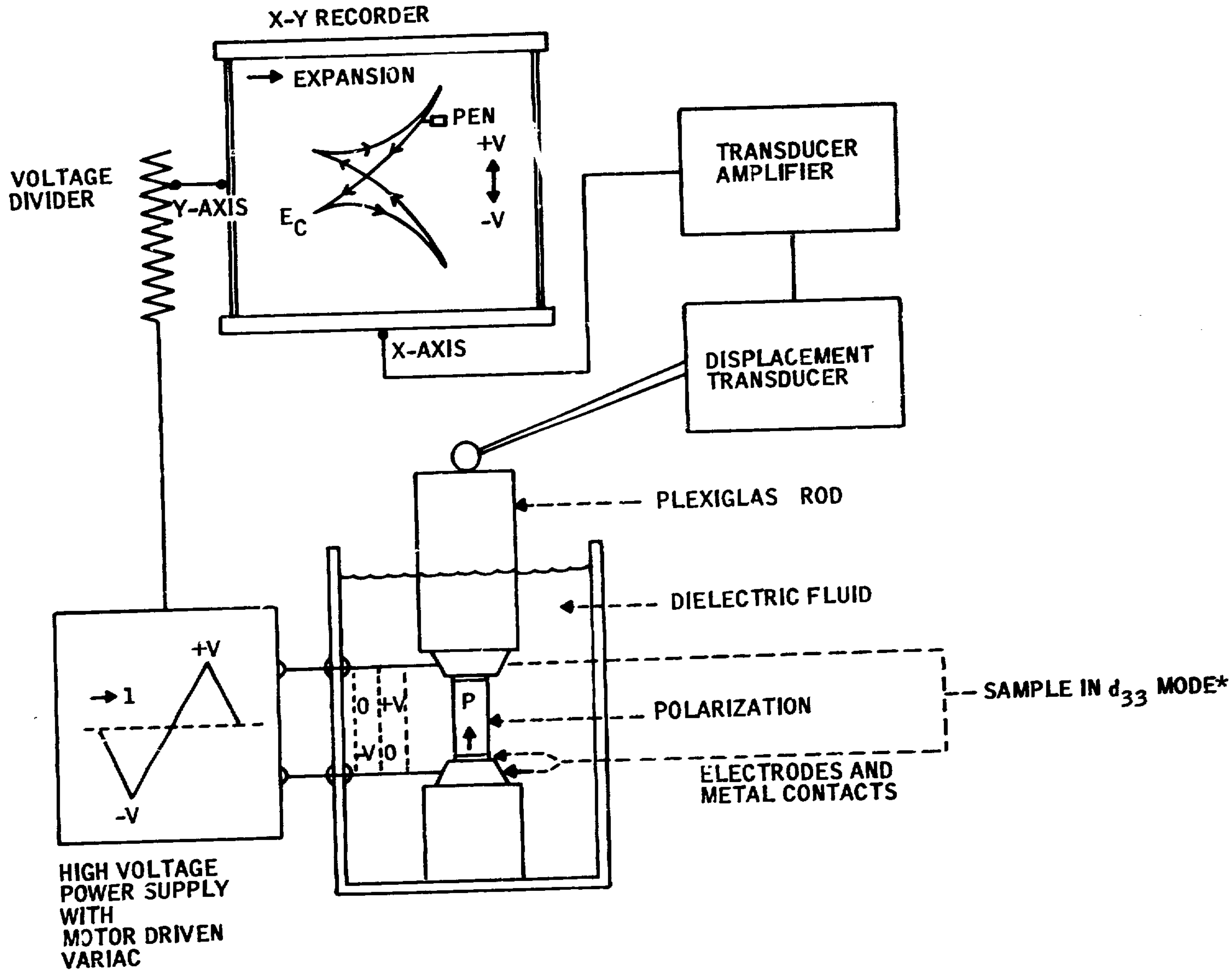


Figure 6. Field versus extension test apparatus.

Table 3. High voltage strain constants for experimental material.

Material	Average Atomic Mass	Field V/mil	d_{33} m/v(10^{-12})	d_{31} m/v(10^{-12})	d_{15} m/v(10^{-12})
Hot Pressed K-13 PZ-PT	65	35	+428	-219	-125
Type 101 $BaTiO_3$	46	35	+228	-85	-76
Type 113 $BaTiO_3$	46	35	+134	-47	-24
Rochelle Salt	10	35 35	-48 +24	+147 -4	
TGS	10	133		-30	
$(Sr_{0.5}Ba_{0.5})Nb_5O_{15}$	44	35	+81		
$LiNbO_3$	30	35 76	+23 +51		
$LiGaO_2$	27	35 87	-4 -9		
Ta O_3	53	35 100	+1 +12		

direction, voltage was applied and extension was measured in the original polarization direction (d_{15}). The electrode set up is shown in the inset of Figure 7.

RESULTS AND DISCUSSION

Figures 8 to 13 show the typical field versus extension plots for the experimental materials evaluated in this program. Figure 8 shows the full loop behavior of the presently used Honeywell hot-pressed K-13 PZ-PT and two possible substitutes, type 101 and 113 $BaTiO_3$. These show the percent extension in thickness of a part (d_{33}-mode) where voltage is initially applied across the thickness in the same direction as the original polarization field and then reversed to reach a negative field which tends to reverse polarization. The resistance to depolarization depends upon the type of doping. The K-13 PZ-PT (acceptor doped with strontium) exhibited very slight switching or depolarization at 35 volts/mil wheras the type 113 and 101 $BaTiO_3$ started to switch at 22 and 12 volts/mil, respectively. The type 113 $BaTiO_3$ (doped with $CaTiO_3$ and $PbTiO_3$) is compounded to have greater field stability but has a lower percent extension than the type 101 $BaTiO_3$. In normal operation positive voltages can be used up to about 80 volts/mil or the breakdown limit of the material and to a negative field which is about 75 percent of the switching field given above. Figures 9 and 10 show half loops for three operational modes--d_{33}, d_{31} and d_{15}. These data are also summarized in Table 3 for a comparable field of 35 volts/mil. Note that while the Type 101 $BaTiO_3$ has almost twice the output of the type 113 $BaTiO_3$, the latter material has lower hysteresis and a higher switching field and thus higher stability.

The six other experimental materials evaluated are shown in Figures 10 to 12; most of these had significantly less field versus strain capability as compared to the $BaTiO_3$.

Rochelle salt as shown in Figure 11 does show a very high d_{31} strain (157×10^{-12} M/V) which would be desirable for a disc type PLC transducer and the average atomic mass was 75 percent less than $BaTiO_3$, but is quite moisture sensitive. Also the hydroxyl ions in this material are expected to make it quite sensitive to radiation degradation.[25] As shown in Figure 12, Triglycine sulfate had a threshold field of about 40 volts/mil which had to be exceeded before any appreciable

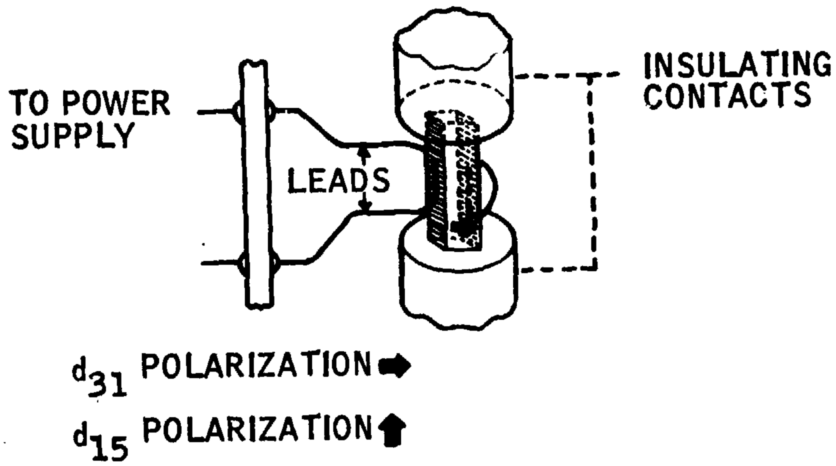


Figure 7. Set-up transverse (d_{31}) or shear (d_{15}) modes.

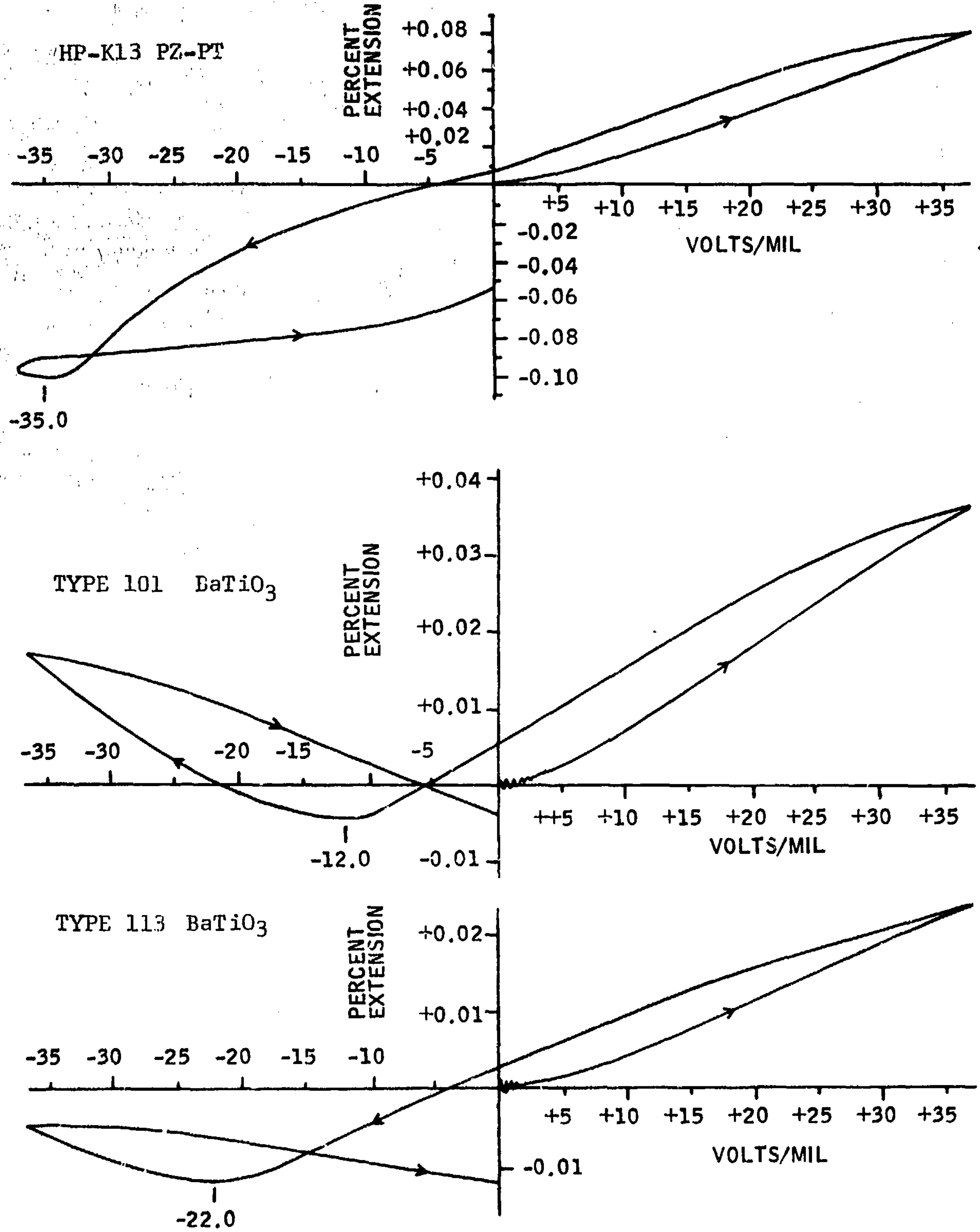


Figure 8. Field versus extension PZ-PT and $BaTiO_3$ 33 mode.

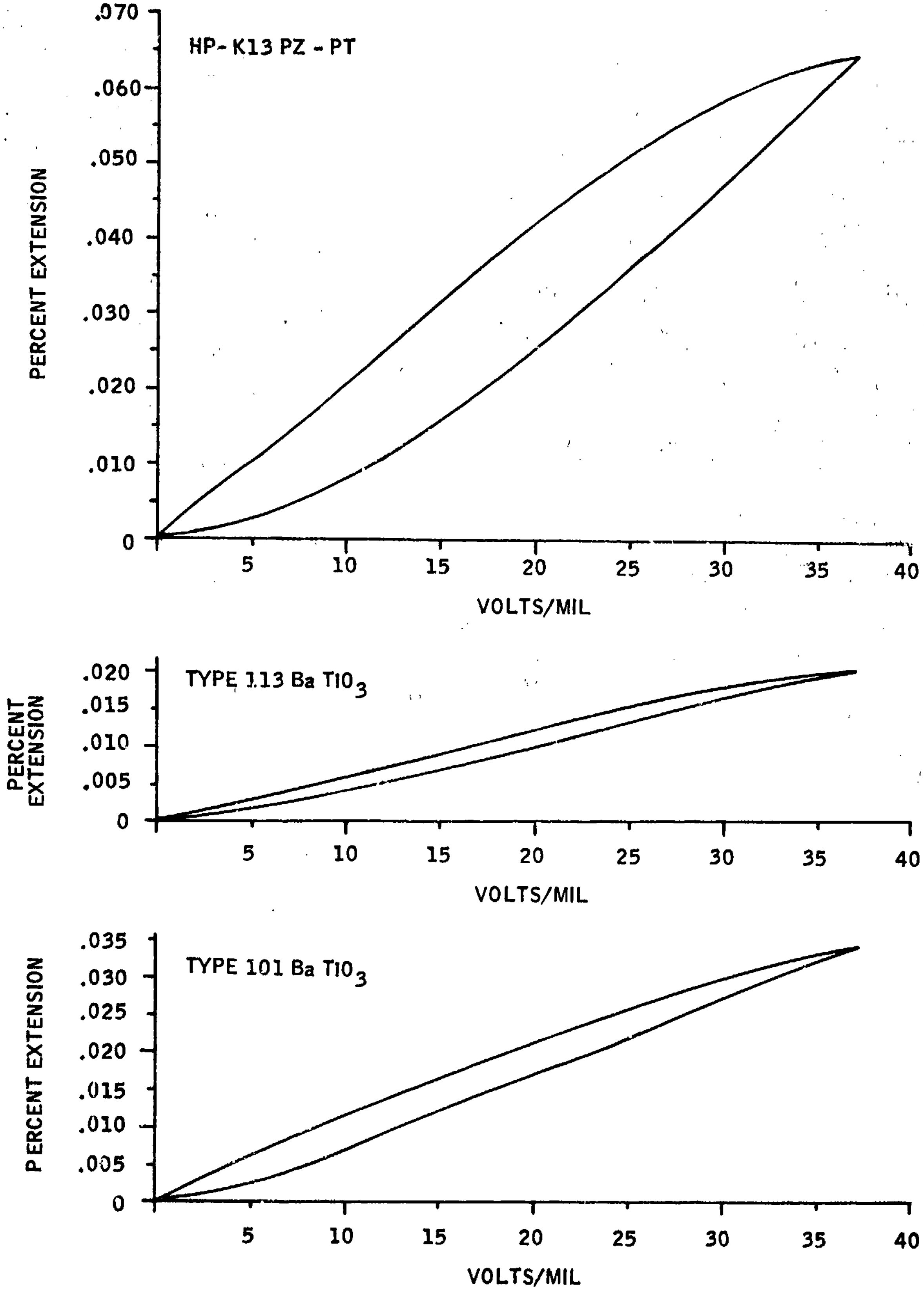
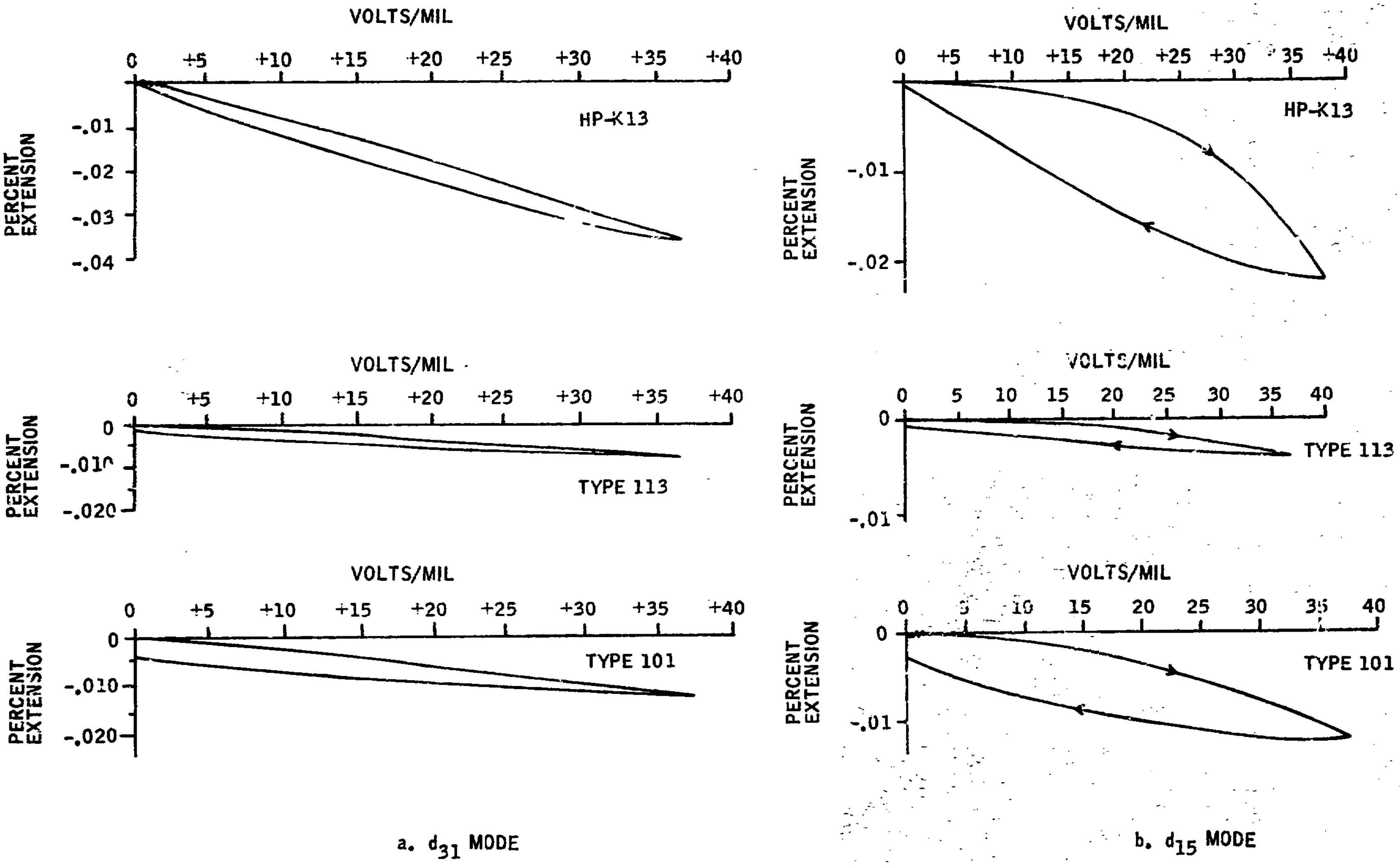


Figure 9. Field versus extension (half loop) poled material d_{33} mode.



a. d_{31} MODE

b. d_{15} MODE

Figure 10. Field versus extension (half loop) for poled material.

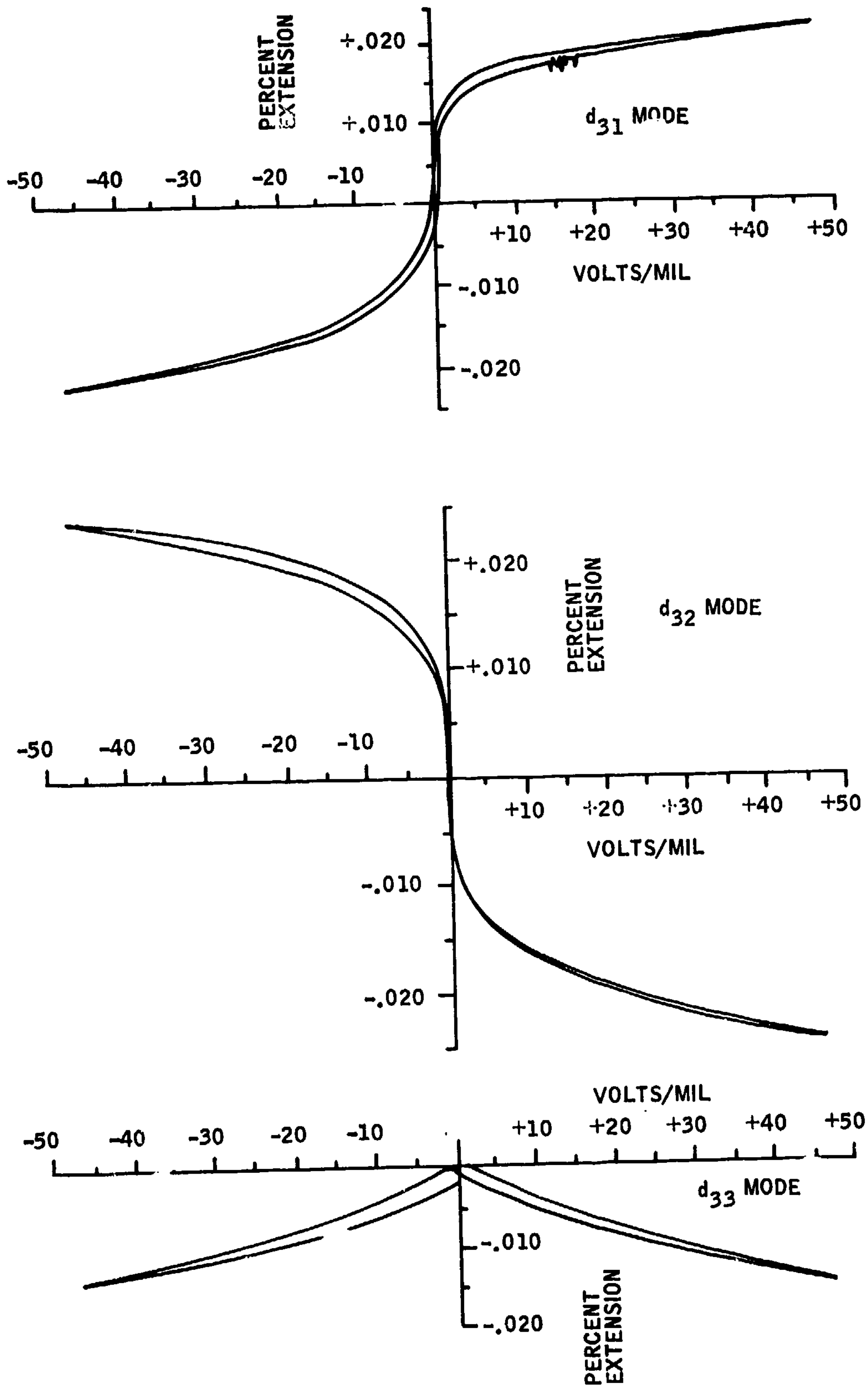


Figure 11. Field versus extension of single crystal Rochelle salt.

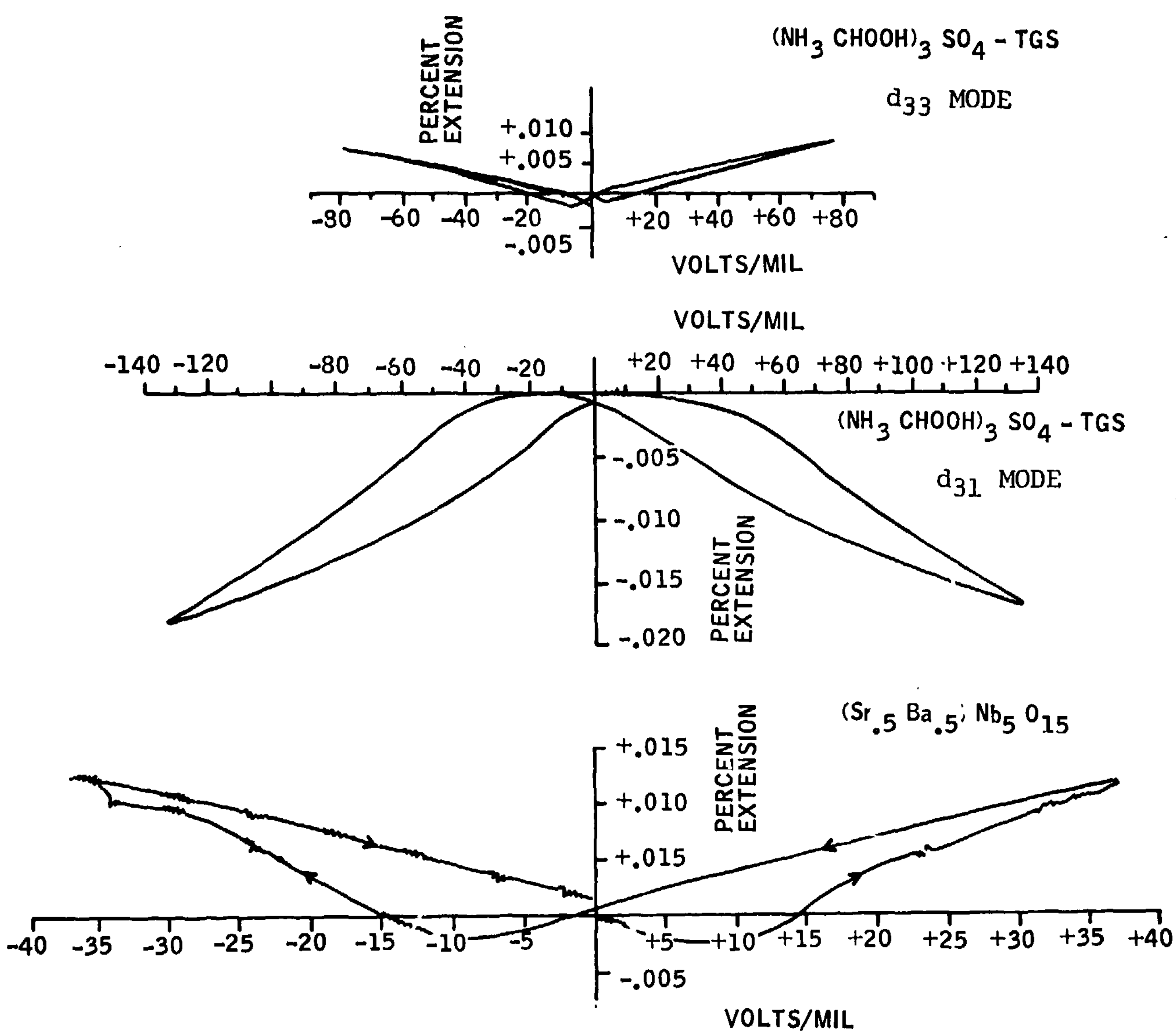


Figure 12. Field versus extension character of $(Sr_{.5}\ Ba_{.5})$ Nb_5O_{15} and $(NH_3CHOOH)_3\ SO_4$.

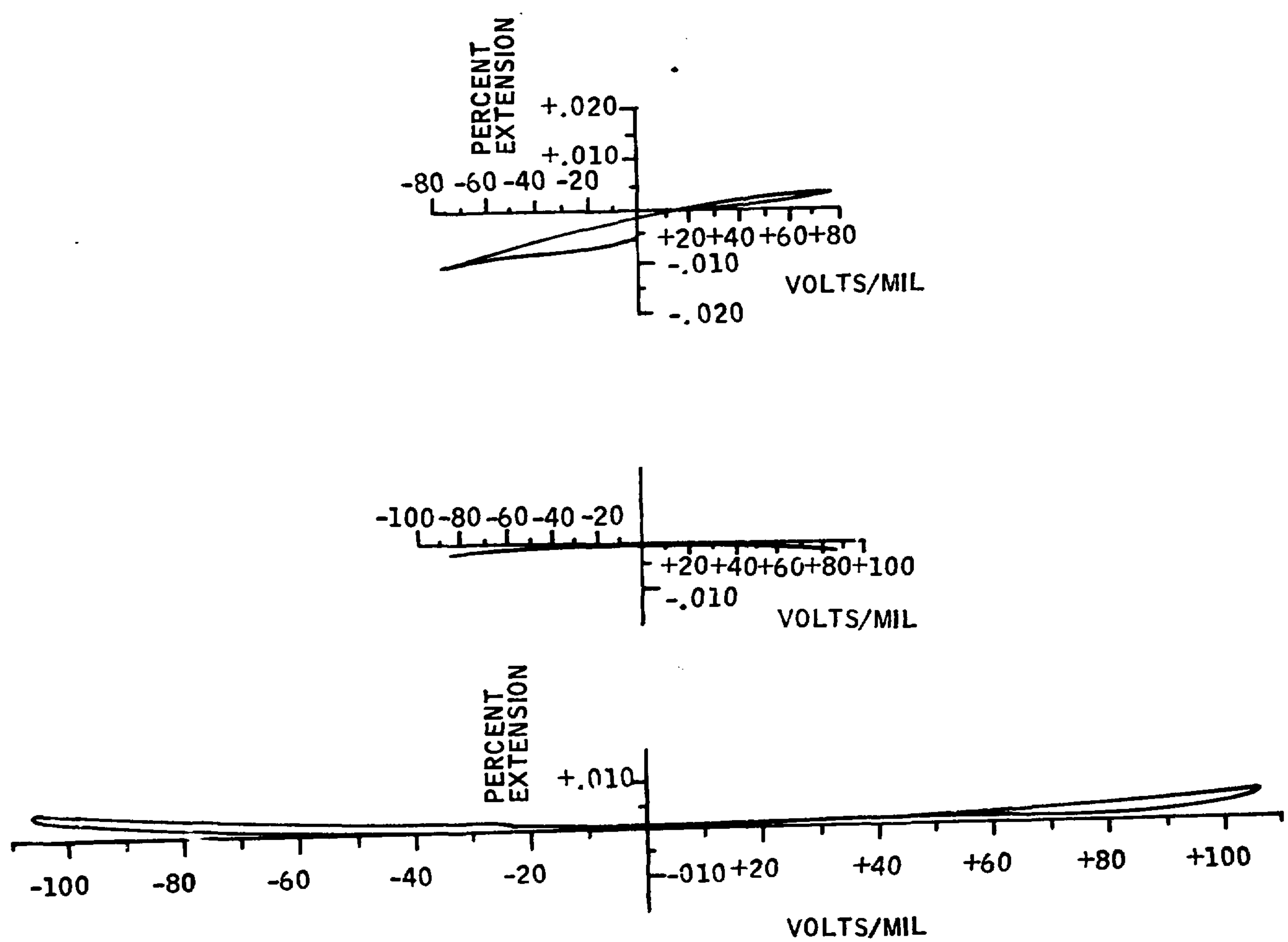


Figure 13. Field versus extension character of $KTaO_3$, $LiNbO_3$ and $LiGaO_2$ d_{33} mode.

strain was produced in the d_{31} direction. Figure 12 also shows data for a $(Sr_{0.5}Ba_{0.5})Nb_5O_{15}$ (SBN) single crystal which had fairly high d_{33} expansion; and the average atomic mass was slightly less than PZ-PT, but large crystals are very difficult and costly to produce. Figure 13 shows the low displacements obtained for the other three materials.

The materials which appear to offer the most promise are the $(K_{0.5}Na_{0.5})NbO_3$ and $(Na_{0.8}Cd_{0.1})NbO_3$ type ceramic materials with a Z of 34. The d_{33} of these materials may exceed 200, their Curie temperature is much higher than $BaTiO_3$ (Z of 47) and their molecular structure contains no hydroxyl ions. Additional efforts are necessary to attempt to make ceramic formulations of these NbO_3 base piezoelectric ceramic materials.

Radiation Resistance

The radiation resistance of many of these materials has been studied previously, however, we were unable to find any work that studied more than one type of ferroelectric type material at a time.

Ruffing[17] summarizes the effort in electrical materials. In general, metals where electron mobility is quite high take very large amounts of radiation energy to produce any significant structural changes other than heating. In organic materials, physical or chemical deterioration usually takes place before appreciable changes in electrical properties occur. Radiation resistance does depend strongly on the temperature capability of the material because induced heating can destroy cross-linked and chain-scission type organics such as a PVF_2 polymer. Doses up to 10^5 rads usually show little or no effect after radiation but electrical resistance in polymers can decrease 100-1000 times during radiation. Ruffing indicates that epoxies are only good to about 10^6 rads without fillers but improve (10^7 - 10^8 rads) with fillers. Also, mica is reported to be damaged by x-rays (210 KV and 20 ma) where destruction of secondary bonding at crystal faces was caused by the loss of free OH groups. The formation of f-centers and free electrons were put into the crystal lattice at defects.

As discussed earlier, it appears that peculiar changes in the polarization behavior of these materials occur when they are exposed to ionizing radiation (x-rays and

electrons). Most of these changes do not appear to be permanent except possibly where weak, chemically bound hydroxyl materials are present in the crystal structure such as in Rochelle salt.

In all of the articles reviewed[25-33] concerning the radiation resistance of PZ-PT[28, 29] and other piezoelectric type materials, the authors have shown significant changes occur in remnant and saturation polarization and coercive field (this was referred to as switching field earlier). In single crystal materials such as $BaTiO_3$,[27] TGS,[26] Rochelle Salt,[25] and $(NaK)NbO_3$[33] polarization versus field loops were deformed and double hysteresis loops appeared for fast neutron dosages above 10^{12} nvt. This effect was also seen in TGS subjected to ionizing radiations (x-rays and electrons) from an x-ray tube running at only 30 KV and 20 ma and to a detectable degree even at an 8 KV and 15 ma level after several hours. Chynoweth[26] suggests that the effects are caused by the gradual increase of strain in the crystal.

In general, as exposure times are increased, the coercive field (E_c) decreases and eventually polarization decreases. Since the amount of polarization present is directly related to the piezoelectric strain constant, the displacement in a PLC type transducer will be decreased.

The effects noted are somewhat typical of simple heating of these crystals. For instance, when PZ-PT is heated, E_c decreases and polarization decreases as the Curie temperature is approached. In certain mixed phase PZ-PT structures, a double hysteresis loop may also be obtained. Thus, simple heating by ionization radiations is expected to be the primary cause of PLC instability in the laser gyro. The properties which need to be modified are:

- Reduction of the average atomic mass which will decrease the amount of radiation induced heating.

- Increasing the temperature stability of the piezoelectric properties to improve the micropositioning stability of the transducer. This can be obtained by:
  - Increasing the Curie temperature
  - Increasing the coercive field
  - Stabilizing d_{33} and d_{31} outputs with temperature.

RECOMMENDATIONS

The best material presently available for this purpose is probably type 113 $BaTiO_3$ or a temperature stable PZ-PT such as used in piezoelectric band-pass filters. Both of these will produce less displacement for a given drive voltage than the presently used hot pressed K-13 PZ-PT; however, design changes in the transducer as discussed below are expected to compensate for these reductions. New materials such as $(Na_{0.5}K_{0.5})NbO_3$ and $(Na_{0.8}Cd_{0.1})NbO_3$ or combinations of these also should be more thoroughly evaluated for their field versus train temperature stability. This is also particularly important because it would improve the functional stability of the gyro over other non-radiation sensitivity improvements.

PLC TRANSDUCER DESIGN

Seven potential design configurations for the path length control (PLC) transducer have been initially examined which could utilize the new low Z materials analyzed under this program. Seven representative design configurations are shown in Figure 4 and Figures 14 through 18. These take several different approaches to the problem and can be combined as desired to achieve maximum benefits.

In all these designs, a standard method of electroding is shown. The piezoelectric ceramic shapes contain fired silver electrodes. External electrical contacts are achieved by cementing a thin metallic electrode to the silver which can be soldered to copper lead wires.

Since the existing design is the one which is known the best, it will be used as the control as well as a potential candidate for future application. The only change is to reduce the diaphram thickness to permit greater throw with piezoelectric materials with lower d_{31} or less throw efficiency. This configuration is shown in Figure 4. A variation in this design is shown in Figure 13 where the driver assembly is bonded to the transducer (mirror) instead of using a mechanical linkage. This should produce greater throw efficiency; however, previously used bonded structures of this type have experienced bond failures.

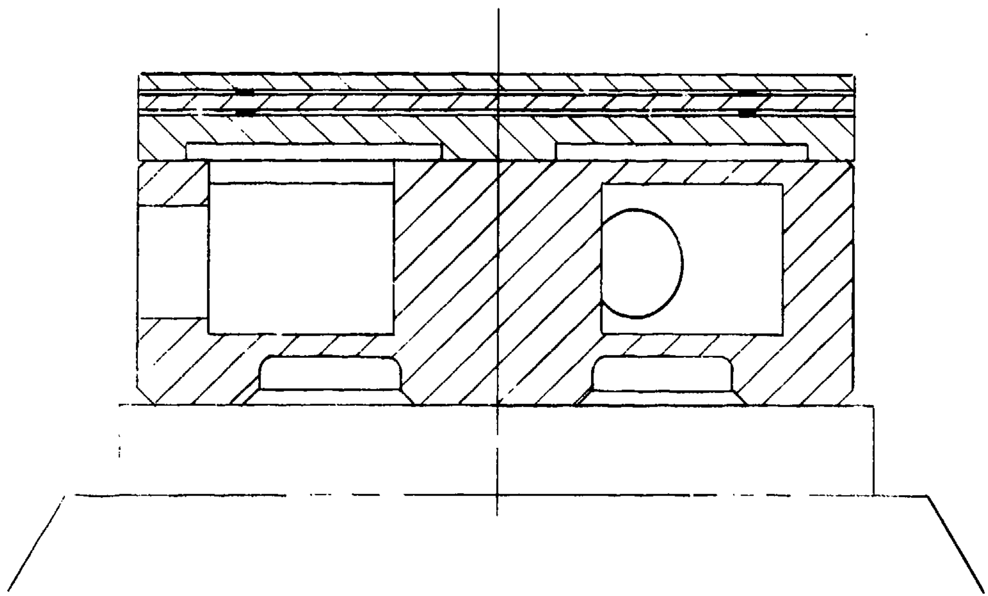


Figure 14. PLC transducer - cemented configuration.

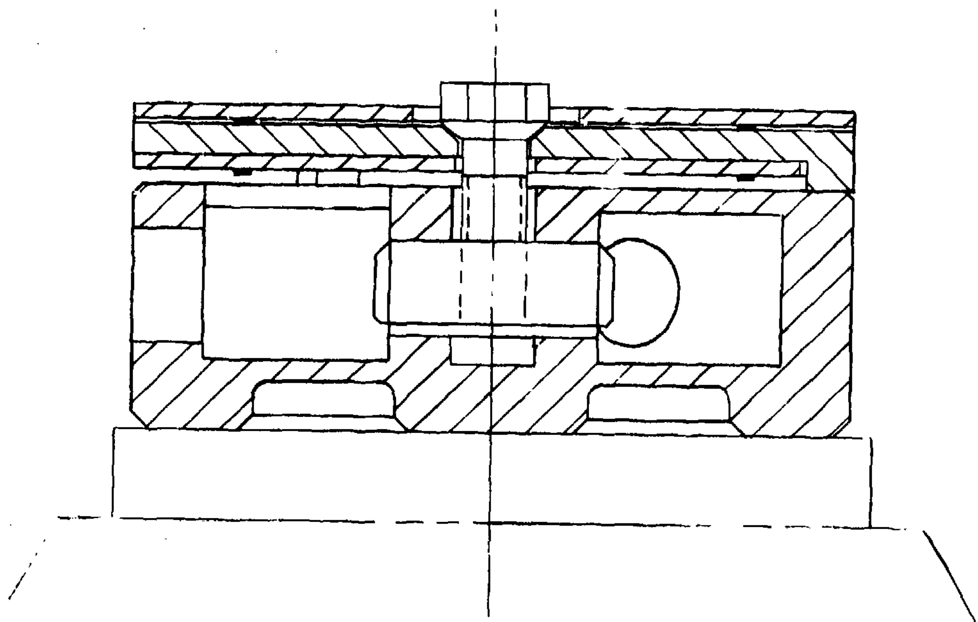


Figure 15. PLC transducer - top and bottom driver.

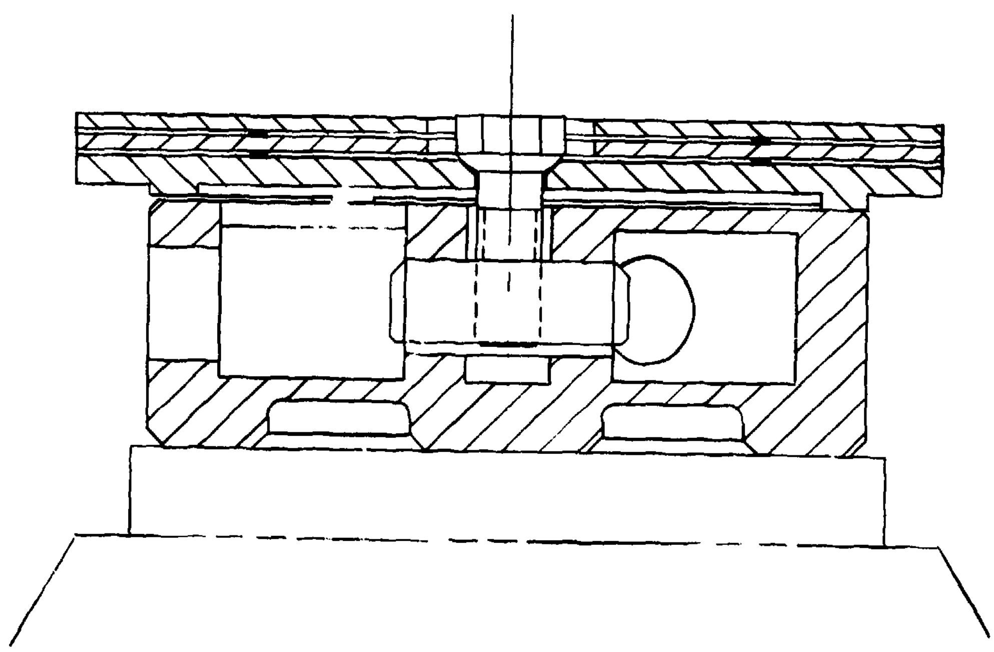


Figure 16. PLC transducer - large diameter driver.

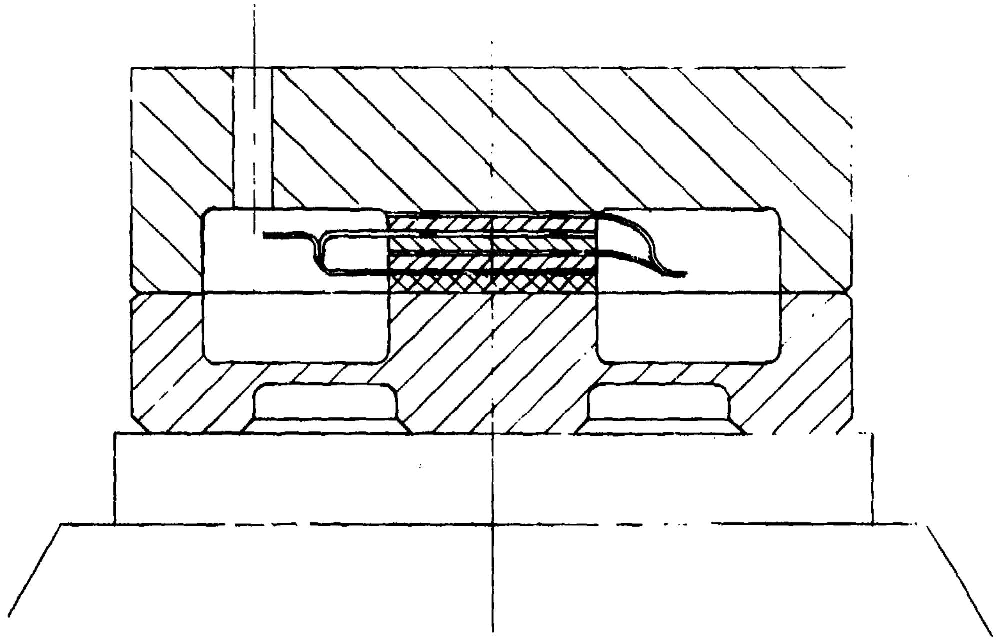


Figure 17. PLC transducer - d_{33} center stack.

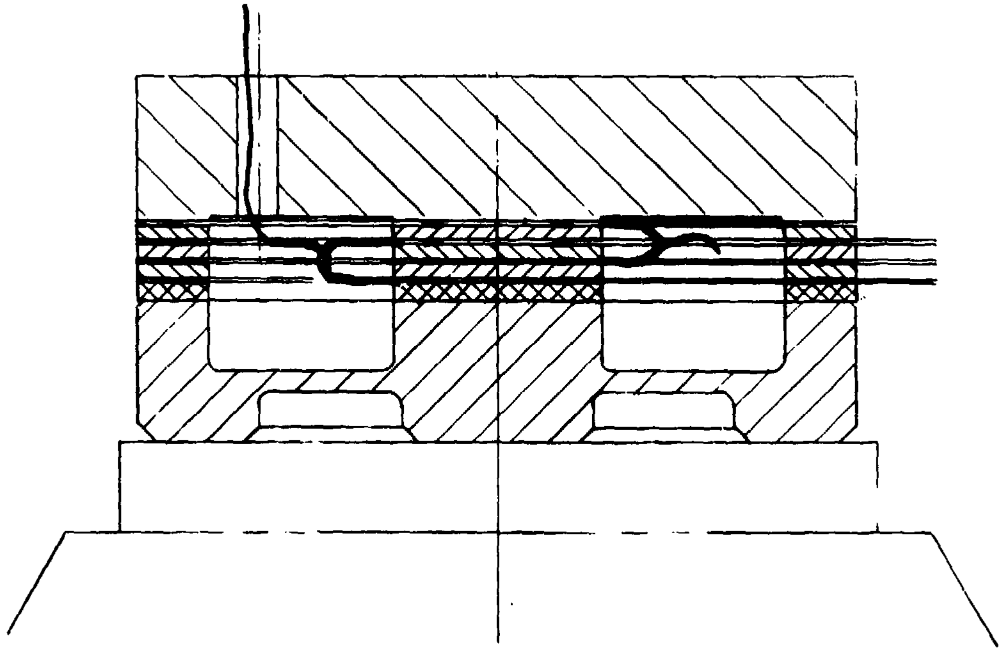


Figure 18. PLC transducer - d_{33} center and washer stacks.

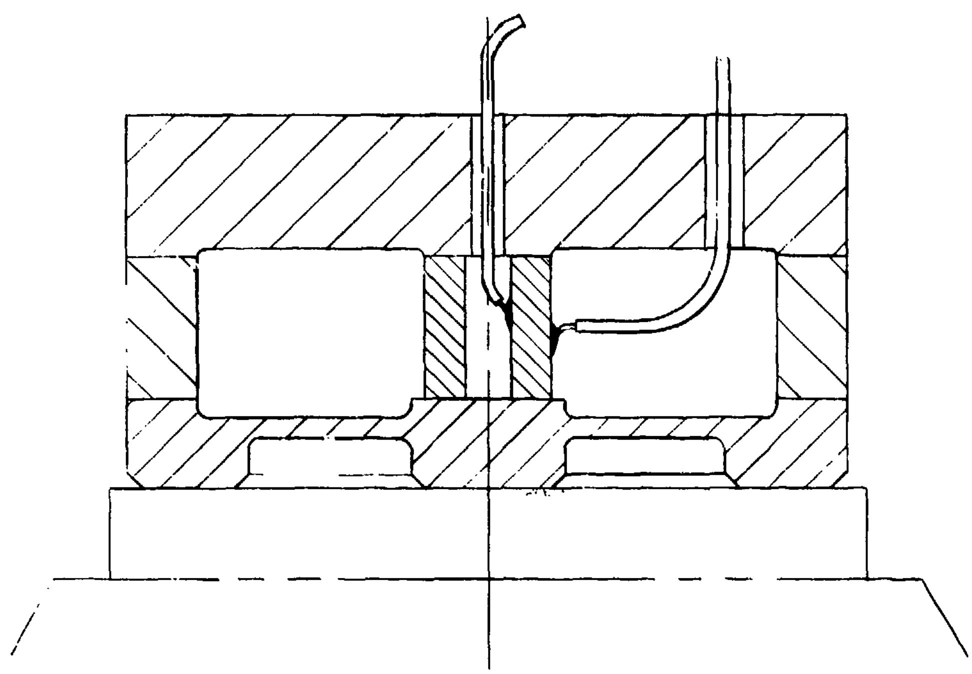


Figure 19. PLC transducer - d_{31} center cylinder.

Since the apparent result of the radiation in causing a failure mode is to absorb radiation, the present effort has concentrated on finding less absorptive material. However, since the heating deformation action is the real failure causing mode, design changes can be made to mitigate this result. Top and bottom mounted piezoelectric elements would both tend to heat as a result of radiation and their temperature increase would tend to compensate or cancel the motion-producing effect. An approach which uses this technique is shown in Figure 15. A variation of this technique would be to use a single crystal as the driver to reduce the bimetallic effect from the present two layer sandwich.

Another approach would be to utilize two separate PLC transducers each thermally compensated to move in opposite directions to provide total path length-compensation. This design may be more difficult to control and evaluate, for which reason it will not be considered in this study.

Since the most significant anticipated result of using a low Z piezoelectric material is lower throw efficiency, another technique would be to increase the area of the crystal(s) to obtain greater throw. Approximately 50 percent increase in crystal area can be achieved without the device becoming excessively large. There is the trade off, however, which must be made of increased area (i.e., material), and sensitivity to irradiation even though the Z number is reduced. A representation of this approach is shown in Figure 16.

Another class of driver is shown in Figure 17. It utilizes the expansion/contraction of a piezo stack for direct actuation of the mirror. The internal version would benefit from additional shielding inside and/or outside the transducer. Also, its small volume would minimize radiation absorption. An approach which is more complicated, but holds promise of both greater throw and self compensation from heating is shown in Figure 18. Here the crystal heating resulting from irradiation will tend to cancel the resulting motion of the element stacks. The normal operation of push/pull should also amplify motion from available voltages to maximize throw.

The effect of shear poling was demonstrated during the first phase of this program and gives rise to the device shown in Figure 16. The slug has been refined to a hollow cylinder. It is shown in a similar design to the inside element stack of Figure 17. Its simplicity is attractive. The use of inside/outside cylinders for thermal compensation and maximized throw would probably be the better configuration of this type of driver.

The versions proposed for study in any future effort include 1) the top and bottom element standard design, 2) the internal/external stack and 3) the internal/external d_{15} or d_{31} poled cylinder approach.

These self-compensating versions appear to hold the most promise of thermal insensitivity both to normal and radiation environments.

SECTION 3
CONCLUSIONS

Three lower average atomic mass piezoelectric ceramic materials were identified in this program which appear to have sufficient field-versus-displacement to be used in place of the present lead zirconate-lead titanate in the driver section of the path length control (PLC) transducer. Sodium potassium niobate and sodium cadmium niobate have about one half the average atomic mass of the presently used material while the more common barium titanate materials are two-thirds less. Both materials have lower displacement coefficients (d_{31}) but more efficient transducers have been designed which appear to compensate for this lower motion. While many other materials were identified which had significantly lower average atomic masses, their displacement coefficients were too low to be of use in the transducer. One material, TGS containing hydroxyl ions, may also deserve further study because the radiation sensitivity of this material is not well known.

SECTION 4
RECOMMENDATIONS

It is recommended that two types of $BaTiO_3$ be used to study the performance of these two materials in at least three new PLC transducers. Prototype models of these designs should be built and evaluated to determine their path length control capability. Simultaneous to this effort, a standard hot pressing process should be used to produce the sodium potassium (and cadmium) niobate piezoelectric ceramic elements. The actual displacement characteristics of these should be optimized and this material should then be evaluated and compared to single crystal TGS in the most appropriate design found with the $BaTiO_3$. The function of a laser gyro with these prototype PLC transducers should then be evaluated under ambient and a high radiation environment.

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